

Table 3. Summary of the results of magic integers for hexahelicene

		Set A	Set B	Refined phases		Published
		$x=0.103$ $y=0.887$	$x=0.085$ $y=0.904$	Set A	Set B	phases
ϕ_1	$2x$	74	60	44	50	75
ϕ_2	$3x$	111	91	71	81	57
ϕ_3	$7x$	259	213	249	223	274
ϕ_4	$13x$	122	36	132	126	155
ϕ_5	$2y$	278	290	298	310	323
ϕ_6	$3y$	238	255	258	265	198
ϕ_7	$7y$	75	116	115	126	184
ϕ_8	$13y$	193	268	182	188	119
ψ/n		0.72	0.64	0.99	0.99	
Mean deviation from published phases		46°	67°	40°	42°	

Conclusions

We have shown that by the application of magic integers it is possible to allocate phases to a starting set of reflexions in a less arbitrary manner than by the phase-permutation method. The resulting saving in the number of sets of phases to be developed may well be significant for structures that require a large starting set to obtain a solution. As a rough estimate, the time required for the magic-integer and refinement procedures is about the same as that required for the development of one or two complete sets of phases. Normally the number of peaks in the ψ map is not too great and different peaks sometimes give virtually the same values for the individual ϕ 's. For structures for which

MULTAN gives a solution by the permutation of phases then the use of magic integers can give a saving of computer time of between 50 to 75%. In those cases where the convergence map gives poor phase development the phase-permutation method may be quite impossible and the magic-integer approach is then extremely valuable.

The method is currently being developed by trying to accept a limited number of \sum_2 relationships before the allocation of magic integers. This is aimed at including more \sum_2 relationships in the map and enabling about 30 or 40 reflexions to be phased. At present the procedure is handled by a separate computer program which is run between the *CONVERGE* and *FASTAN* procedures in *MULTAN*. A magic-integer routine will eventually be incorporated as an option in the *MULTAN* package.

We wish to express our gratitude to the Science Research Council for support of this project and also to the Department of Computer Science of the University of York for computer services. One of us (M.M.W.) is grateful to his colleagues for lack of distraction during the Board of Studies in which this idea was first conceived.

References

- DECLERCO, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A29, 231–234.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–375.
 KARLE, I. L., KARLE, J. & ESTLIN, J. A. (1967). *Acta Cryst.* 23, 494–500.

Acta Cryst. (1975). A31, 56

The Effect of Coulombic Interactions on the Calculated Crystal Structures of Benzene at Atmospheric and 25 kbar Pressure

BY DAVID HALL

Department of Chemistry, University of Auckland, Auckland, New Zealand

AND DONALD E. WILLIAMS

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208, U. S. A.

(Received 1 April 1974; accepted 15 May 1974)

The crystal structures of benzene I (orthorhombic) and high-pressure benzene II (monoclinic) were calculated at atmospheric pressure and 25 kbar pressure by minimization of the intermolecular lattice energy subject to the pressure constraint. The first set of calculations used an atom-atom (exp-6) potential with no net coulombic charges on the atoms. The second set of calculations used an (exp-6-1) potential which placed charges of ± 0.18 electron on each atom of the benzene molecule. The no-charge calculation incorrectly predicted that benzene should be monoclinic at both atmospheric and 25 kbar pressure. The coulombic charge calculation correctly predicted the observed crystal transition, favoring the orthorhombic structure at atmospheric pressure but favoring the monoclinic structure at 25 kbar. In the latter calculations there were substantial coulombic contributions to the lattice energy.

Introduction

The crystal structure of benzene I has been determined by X-ray diffraction at -3° (Cox, Cruickshank &

Smith, 1958) and by neutron diffraction at -55° and -135° (Bacon, Curry & Wilson, 1964). Since our calculated model does not include vibrational effects, we will compare our results with the observed structure

at -135° . The crystal structure of benzene II has been determined at 21° and 25 kbar pressure by X-ray diffraction (Piermarini, Mighell, Weir & Block, 1969). The low-pressure form is orthorhombic, space group $Pbca$, with four molecules in the unit cell situated on inversion centers. Benzene II is monoclinic, space group $P2_1/c$, with two molecules in the unit cell, also situated on inversion centers.

For both benzene I at -135° and benzene II we have fitted an idealized molecule of perfect D_{6h} symmetry to the observed carbon positions. This idealized molecule has C-C and C-H bond lengths of 1.397 and 1.027 Å respectively. Thus, the C-H effective bond length was foreshortened (Williams, 1965) and the hydrogens placed in calculated positions. The orientation matrices for the molecules were obtained by a least-squares fit of the idealized carbon positions to the observed carbon positions in the two structures. Table 1 gives the atomic coordinates and the orientation matrices for the two structures.

Table 1. *The atomic coordinates ($\times 10^3$) of the benzene molecule and the observed molecular orientation matrices* ($\times 10^4$) for crystalline benzene I and benzene II (Å)*

	<i>X</i>	<i>Y</i>	<i>Z</i>	
C(1)	1397	0	0	Benzene I $\begin{bmatrix} -3178 & -6593 & 6814 \\ 9476 & -1950 & 2532 \\ -0341 & 7261 & 6867 \end{bmatrix}$
C(2)	-1397	0	0	
C(3)	699	1210	0	
C(4)	-699	-1210	0	
C(5)	-699	1210	0	
C(6)	699	-1210	0	
H(1)	2424	0	0	Benzene II $\begin{bmatrix} 8056 & -3585 & -4717 \\ 0905 & 8613 & -5000 \\ 5855 & 3601 & 7263 \end{bmatrix}$
H(2)	-2424	0	0	
H(3)	1212	2099	0	
H(4)	-1212	-2099	0	
H(5)	-1212	2099	0	
H(6)	1212	-2099	0	

* For the monoclinic system *X* and *Y* are taken parallel to *a* and *b*.

Method of calculation

All calculations were performed with a modified version of Fortran program PCK6 (Williams, 1972). This program was used to minimize the first derivatives of the crystal lattice energy as a function of the three lattice constants and the three molecular rotation angles as required by the symmetry of these structures. The effect of pressure was included in the program by targeting the first derivatives of the lattice energy with respect to *a*, *b*, and *c* to the appropriate values for 25 kbar hydrostatic pressure.

To obtain numerical values for the first derivatives of the lattice energy, we note that, neglecting thermal effects

$$-P = \frac{\partial E}{\partial V} = \frac{\partial E}{\partial a} \frac{\partial a}{\partial V} + \frac{\partial E}{\partial b} \frac{\partial b}{\partial V} + \frac{\partial E}{\partial(c \sin \beta)} \frac{\partial(c \sin \beta)}{\partial V}$$

where *X* and *Y* are taken parallel to *a* and *b*. For the case of hydrostatic pressure the three terms on the right-hand side are equal from the equipartition principle. Thus we obtain

$$\frac{\partial E}{\partial a} = \frac{Pbc}{3}, \quad \frac{\partial E}{\partial b} = \frac{Pac}{3}, \quad \text{and} \quad \frac{\partial E}{\partial c} = \frac{Pab \sin \beta}{3}.$$

The appropriate pressure units are kJ/mole Å³ to obtain the derivatives in units of kJ/mole Å. In the calculations for benzene II the monoclinic angle was held to the value observed at 25 kbar pressure. In the low-pressure calculations, 1 atm pressure does not differ significantly from zero pressure.

Each calculation was carried out in duplicate with two different sets of nonbonded potential parameters (Table 2). Set *A* corresponds to set *C* of Williams (1970). This set is composed of (exp-6) potentials for C...C, C...H, and H...H interactions as derived by least squares from 18 observed hydrocarbon crystal structures, including benzene I. Potential set *B* was derived from the same experimental data, but the potentials are of the (exp-6-1) type which include interactions between point charges on the atoms of different molecules (Williams, 1974). The optimum fit obtained with potential set *B* was better than that for potential set *A*, with resulting values of $\pm 0.179 e$ being obtained for the point charges. It was noted that benzene I has an unusually large coulombic contribution to its lattice energy. Both set *A* and set *B* potentials assume that the geometric-mean combining law holds for attraction; set *B* further assumes that the geometric-mean combining law holds for repulsions.

Table 2. *Nonbonded potential parameters*

(kJ/mole, Å, and electron units), where
 $E = B \exp(-Cr) - Ar^{-6} + q_j q_k r^{-1}$

Parameter	Set A	Set B
A_{CC}	2.14×10^3	1.88×10^3
A_{HH}	1.02×10^2	1.68×10^2
B_{CC}	3.00×10^5	2.99×10^5
B_{CH}	3.56×10^4	geometric mean
B_{HH}	9.08×10^3	1.20×10^4
C_{CC}	3.60	3.60
C_{HH}	3.74	3.74
q_C	0.0	-0.179
q_H	0.0	+0.179

All lattice-energy calculations used the convergence-acceleration technique (Williams, 1971). The direct lattice sums were evaluated up to 8 Å. The convergence acceleration separation constants K_1 and K_6 were set to 0.2, and the reciprocal sum was neglected. The error in the r^{-6} lattice summation with $K = 0.2$ is given by Williams (1971) and is less than 1%. For the coulombic sums we tested the value $K_1 = 0.2$ with the sodium chloride structure, summing to the 8 Å limit and neglecting the reciprocal sum. The error in the lattice sum was less than 0.1%. Although the unmodified coulombic sum converges more slowly than the un-

modified r^{-6} sum, the convergence-acceleration technique is more effective in the former case.

Results of calculations

Table 3 gives a summary of the numerical results of the calculations. Potential set *A* incorrectly predicts that zero-pressure benzene should be monoclinic. Potential set *B* correctly predicts the orthorhombic form at zero pressure. At 25 kbar pressure both potential sets correctly predict the monoclinic structure.

Table 3. *Benzene crystal structures calculated by molecular packing analysis at atmospheric and 25 kbar pressure*

Structure type	I	I	II	II
Potential set	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
	<i>P=0</i>			
Lattice energy (kJ/mole)	-43.8	-54.2	-45.4	-53.1
Coulombic contribution	0.0	-17.3	0.0	-14.0
Δa (Å)	-0.69	0.04	0.22	0.27
Δb	0.04	-0.13	0.15	0.14
Δc	0.23	0.12	-0.05	0.42
$\Delta\theta$ (°)	17.9	3.5	3.8	1.8
	<i>P=25 kbar</i>			
Lattice energy	-27.7	-37.8	-39.7	-47.0
Coulombic contribution	0.0	-20.4	0.0	-14.5
Δa	-0.88	-0.49	0.04	0.11
Δb	-0.46	-0.46	-0.02	0.02
Δc	-0.45	-0.40	-0.46	-0.13
$\Delta\theta$	18.4	3.4	5.2	2.6

Thus additional evidence is furnished for the superiority of the set *B* potentials over the set *A* potentials. The inclusion of coulombic interactions in crystalline benzene by the set *B* potentials allows the prediction of the orthorhombic-to-monoclinic transformation in this substance.

Both benzene I and benzene II have highly significant coulombic lattice energy when potential set *B* is used. The coulombic contribution to the calculated lattice energy is 32% for benzene I and 26% for benzene II, as obtained with potential set *B*. The coulombic

energy is unusually large in benzene and this fact may be related to the observation that neither naphthalene nor anthracene are observed in the type I orthorhombic structure. Naphthalene and anthracene have the type II monoclinic structures, but with a slightly smaller coulombic lattice energy component than benzene II.

Table 3 also provides additional structural evidence for the superiority of potential set *B* over set *A*. The calculated structures using set *B* have better lattice constants and molecular positions. Thus for benzene I at zero pressure, the largest lattice constant difference is -0.13 Å for potential *B* but -0.69 Å for potential *A*. The molecular orientation is off by 3.5° with set *B* but is off by 17.9° for set *A*.

For benzene II at 25 kbar, the largest lattice constant difference is -0.13 Å for set *B* but is -0.46 Å for set *A*. The molecular orientation is off by 2.6° with set *B* but is off by 5.2° for set *A*.

In conclusion, we have shown that molecular packing analysis (Williams, 1972) can successfully predict the transition from benzene I to benzene II at 25 kbar pressure, using potential set *B*. This potential requires net point charges of $\pm 0.18 e$ on the carbons and hydrogens of the benzene molecule.

This work was supported by research grant GM 16260 from the U.S. National Institutes of Health.

References

- BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. Roy. Soc. A* **279**, 98-110.
- COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. Roy. Soc. A* **247**, 1-21.
- PIERMARINI, G. J., MIGHELL, A. D., WEIR, C. E. & BLOCK, S. (1969). *Science* **165**, 1250-1255.
- WILLIAMS, D. E. (1965). *J. Chem. Phys.* **43**, 4424-4426.
- WILLIAMS, D. E. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 21-34.
- WILLIAMS, D. E. (1971). *Acta Cryst.* **A27**, 452-455.
- WILLIAMS, D. E. (1972). *Acta Cryst.* **A28**, 629-635.
- WILLIAMS, D. E. (1974). *Acta Cryst.* **A30**, 71-74.